



Transesterification of *Jatropha curcas* oil and soybean oil on Al-SBA-15 catalysts

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ABSTRACT

Al-SBA-15 samples with molar Si/Al ratios of 3, 22 and 73 were synthesized and tested for the acid-catalyzed transesterification of *Jatropha curcas* oil with methanol. Being non-edible, low-cost and acidic, *Jatropha* oil is an interesting feed for biodiesel production, as its use would not entrain competition between food and fuel markets. For fundamental reasons, soybean oil, a typical high quality feed, was also investigated, as its negligible free fatty acids content would not mask the extent of transesterification by the simultaneous occurrence esterification. All the catalysts were characterized as to their composition, structure and texture by ICP-AES, ^{27}Al MAS NMR, X-ray diffraction and nitrogen physisorption. Surface acidity was assessed by ammonia adsorption microcalorimetry. The nature of the organic material adsorbed/trapped on the catalyst during reaction was determined by GC-MS after solvent extraction. The possibility of recovering the activity of the catalyst after a reaction cycle was also checked. In the case of soybean oil, the best-performing catalyst was that with Si/Al = 3 (90 mol% fatty acids methyl esters yield at 180 °C, reaction time 24 h, methanol/oil ratio 12). In the case of *Jatropha* oil, the three catalysts showed a virtually identical performance (ca. 100 mol% methyl esters yield at 180 °C, reaction time 24 h, methanol/oil ratio 12), in spite of their remarkable differences in terms of both concentration and strength distribution of the acid sites. Esterification of the free fatty acids present in the feed occurred in parallel to triglycerides transesterification, both reactions being catalysed by the acid sites of the catalyst, as well as by the acids present in the feed. Several secondary reactions occurred during the transformation of both soybean oil and *Jatropha* oil. The corresponding reaction pathways were outlined.

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1. Introduction

Vegetable oils and animal fats are a renewable feedstock for the manufacture of fatty acid methyl esters (FAMEs), which represent a safe, non-toxic and biodegradable alternative to conventional diesel fuel [1]. The process relies on the catalytic transformation of the triglycerides (TGs) into FAMEs by transesterification with methanol and is carried out at the commercial scale by using homogeneous alkaline catalysts. The replacement of such alkaline catalysts with environmentally friendly heterogeneous ones, which do not require costly catalyst neutralization and separation steps and are not corrosive [2], has been widely investigated [3–8]. The transesterification of triglycerides can also occur via acid catalysis, though at a slower rate than that observed with alkaline catalysts [9]. In order to avoid the environmental con-

cerns associated with the use of mineral acids, easily removable, reusable and non-corrosive heterogeneous acid catalysts could be used. A major driving force for investigating their performance is the lack of soap formation, which, by converse, would be unavoidable if oils with a free fatty acids (FFAs) content higher than 0.5 wt% were processed over alkaline catalysts, making hence imperative either to pretreat such oils for lowering their acidity or to use non-acidic, costly feedstocks. Though diverse acidic solids have already been investigated as catalysts for the transesterification of vegetable oils, serious drawbacks have been reported for all of them. Thus, remarkably high temperature and reaction time are necessary on zirconia/alumina-supported WO_3 [10], the leaching of sulphate species compromises the reusability of sulphated zirconia [11], the lack of thermal stability is a major problem with ion-exchange resins [12,13], and the hindered diffusion of triglycerides makes the performance of La^{3+} -exchanged Beta zeolites rather poor [14]. Very recently, the combined influence of the catalyst acidity and porosity features on the transterification of soybean oil with methanol has been investigated in detail in the present authors' laboratory [15]. It

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was found that, in comparison with conventional Beta and MCM-22 zeolites of similar acidity, the FAMEs yield over micro/mesoporous hierarchical Beta zeolites was twice to three times higher, as a consequence of the enhanced reactants diffusion in their secondary mesoporous system. In view of the above, Al-SBA-15 seems a good candidate as an acid transesterification catalyst. Its highly ordered mesopore system is characterised by wide pore size and thick pore walls. The latter feature makes the material thermally stable, while the former would allow the reactants to diffuse easily within the catalyst pores. Furthermore, thanks to the possibility of isomorphically substituting Si atoms by Al atoms within a wide range of Si/Al ratio, the acidity of the catalysts could be tuned according to the reaction needs. To the best of the present authors' knowledge, no papers reporting on the use of Al-SBA-15 for such purpose have been published so far. Furthermore, though it is generally assumed that reacting feedstocks with a high FFAs content on acid catalysts would result in the enhancement of the FAMEs yield as a consequence of the simultaneous, acid-catalysed transformation of free fatty acids into esters [16,17], papers reporting on the use of solid acids for the one-step processing of FFA-containing oils are rare [18].

The present paper deals with the use of Al-SBA-15 catalysts for the transesterification of soybean and *Jatropha curcas* oils with methanol. Al-SBA-15 samples with a molar Si/Al ratio of 3, 22 and 73 were synthesized and characterized as to their structure by X-ray diffraction (XRD) and ^{27}Al MAS NMR spectroscopy, while nitrogen physisorption was used for assessing the textural properties of the catalysts. The acid features of the samples were investigated by adsorption microcalorimetry using ammonia as a basic probe molecule. By the simultaneous determination of the adsorbed amount and the heat evolved at increasing coverage, such technique is able to assess both the concentration and the energetic features of the acid sites [19–22]. The catalytic behaviour of the Al-SBA-15 samples was investigated by reacting each oil (soybean or *Jatropha*) with methanol in a stainless steel autoclave reactor operated at 180 °C and 4 MPa. *Jatropha* oil was considered worthy of study in view of its great potential as a raw material for biodiesel manufacture [23]. Being non-edible, there would be no competition between food and fuel markets. Furthermore, the *Jatropha* plant, whose seeds contain up to 40 wt% of oil, is well adapted to poor soils and harsh climate conditions. It is hence a good candidate for cultivation in wastelands, where it would help eco-restoration. Soybean oil was selected as a typical high quality feed, in which, due to the negligible FFAs content, the actual extent of the transesterification reaction would not be masked by the occurrence of FFAs esterification. Its investigation was undertaken with a double aim: (i) checking whether the controlled induction of acidity in a mesostructured silica material by the isomorphical substitution of Si by Al atoms would result in an improved catalyst in comparison with already reported catalysts, suffering serious drawbacks such as restricted internal diffusion of TGs, thermal instability, active phase leaching; (ii) understanding whether a threshold value of the acidic strength required for the establishing of the reaction could be quantified, a point so far not addressed in the literature. With the aim of outlining the diverse reactions simultaneously occurring during the soybean and *Jatropha* oil processing, the nature of the organic material retained by the catalyst during the run (generically referred to as "coke") was also determined.

2. Experimental

2.1. Materials

Tetraethylorthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS, 98%), Pluronic P123 triblock copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$), aluminium nitrate

($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98.5 wt%), ammonium hydroxide solution (28% in water, 99.99%), methanol (99.8%), diethyl ether ($\geq 99.8\%$), ethanol (99.8%), *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA, derivatization grade), 1,2,3-tridecanolylglycerol (tricaprin, 99 wt%), sodium hydroxide solution (0.1 M) and hydrofluoric acid (40%), were purchased from Aldrich. Sodium chloride (99.5%) and hydrochloric acid (37%) were provided by Carlo Erba and Merck, respectively.

Jatropha oil was supplied by Vero Energia Italia. Soybean oil was a supermarket shelf product. The fatty acid distribution in both oils was determined as follows: 0.5 g of oil and 2 cm³ of 5 wt% KOH in methanol were mixed in a screw capped vial. The vial was shaken for 30 min at room temperature and the formed methyl esters extracted by adding 2 cm³ of hexane. The upper phase was dried with sodium sulfate and the methyl esters were analyzed with a Gas Chromatograph HP 6890 equipped with a FID. A capillary column (length 30 m, internal diameter 0.25 mm, film thickness 0.25 μm) SupelcowaxTM 10 was used, with nitrogen as the carrier gas. The column oven temperature was set at constant temperature (190 °C) for the whole analysis duration (15 min). The injector and detector temperatures were set at 250 °C and 260 °C, respectively. FAMEs were quantified by means of the internal normalization method. The following fatty acid distributions were obtained: palmitic, 10.42 wt%; oleic, 28.08 wt%; linoleic, 52.78 wt%; linolenic, 5.06 wt%; stearic, 3.66 wt% for soybean oil; palmitic, 15.70 wt%; palmitoleic, 0.85 wt%; oleic, 46.07 wt%; linoleic, 30.81 wt%; stearic, 6.57 wt% for *Jatropha* oil. From such distribution average molar masses of 872.90 g/mol and 292.32 g/mol for soybean oil, and 872.16 g/mol and 291.89 g/mol for *Jatropha* oil were calculated for the vegetable oils and the methyl esters, respectively. The FFAs content, expressed as mg of KOH required to neutralize the free fatty acids in 1 g of oil (acid number), was determined according to the standard ASTM D 974 procedure. Acid numbers of 0.20 mg_{KOH}/g_{oil} (0.10 wt% of FFAs) and 10.98 mg_{KOH}/g_{oil} (5.49 wt% of FFAs) were obtained for soybean oil and *Jatropha* oil, respectively.

2.2. Synthesis of catalysts

Al-SBA-15 catalysts were prepared by a modified two-step "pH-adjusting" method [24] by using $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as aluminium source (instead of NaAlO_2) and a hydrothermal treatment of 48 h. The synthesis of Al-SBA-15 was carried out as indicated in the following. Step 1: 4 g of Pluronic P123, 6.7 g of NaCl and 126 cm³ of 1 M HCl aqueous solution were stirred at 40 °C until the complete dissolution of surfactant. The appropriate amount (8.5 g) of TEOS was then added drop-wise to the above solution and the mixture was kept under magnetic stirring at 40 °C for 24 h. The amounts of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ required to obtain the desired Si/Al molar ratios were then added, followed by magnetic stirring for 24 h at 40 °C. The resulting gel was introduced into a 250 cm³ Teflon-lined stainless steel autoclave and submitted to a first hydrothermal treatment at 100 °C for 48 h. Step 2: the suspension resulting from step 1 was cooled to ambient temperature and then the pH value of the mother liquor was adjusted to 5 with ammonia under stirring. The mixture was submitted to a second hydrothermal treatment in autoclave at 100 °C for 48 h. The solid was separated by filtration, washed with distilled water, dried at 60 °C overnight, and calcined in oven at 550 °C for 5 h (heating rate 4 °C/min).

2.3. Catalyst characterization

The total Si/Al molar ratio of the catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Varian Liberty 200 instrument. Before analysis, a HF solution (40 wt%) was added to a known amount of the sample and the mixture was heated until the solid dissolution. The residue

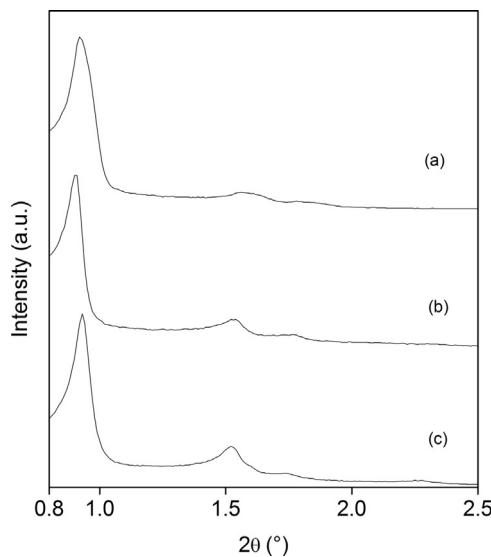


Fig. 1. Low-angle X-ray diffraction patterns for Al-SBA-15(3) (a), Al-SBA-15(22) (b), and Al-SBA-15(73) (c).

remaining after evaporation was solubilized with 2 cm³ of aqua regia and then diluted to a known volume by bidistilled water.

Low-angle X-ray diffraction patterns were recorded on a Seifert X3000 diffractometer with a θ - θ Bragg Brentano geometry using Cu-K α radiation.

High resolution ²⁷Al MAS NMR spectra were collected using a Varian UNITY INOVA Spectrometer with a 9.39 T wide-bore Oxford magnet equipped with a 4 mm probe. The experiments were performed by packing 100 mg of sample in a 4 mm Si₃N₄ rotor at a spinning rate of 7 KHz. Each experiment was run with a recycle time of 500 ms, 90° pulse lengths (6.6 ms) and 5000 scans. ²⁷Al chemical shifts were referenced to Al(NO₃)₃ aqueous solution. Quantitative information on the ²⁷Al atom environments was obtained by fitting the signals with individual Gaussian using the software package Origin 7 from OriginLab Corporation.

Textural analysis was carried out with a Micromeritics ASAP 2020 apparatus by determining the nitrogen adsorption/desorption isotherms at -196 °C. Before analysis, the samples were pretreated overnight under vacuum (10⁻³ Pa) at 250 °C for 12 h. The specific surface area was determined for each catalyst by the BET method. The total pore volume and the pore size distribution (BJH method) were also assessed.

A Tian-Calvet heat flow calorimeter (Setaram) equipped with a volumetric vacuum line was used for microcalorimetric measurements. After calcination at 450 °C for 12 h, each sample (0.1 g) was pre-treated at 250 °C for 12 h under vacuum (5 × 10⁻³ Pa). Adsorption was carried out at 80 °C by admitting successive doses of the probe gas (ammonia) and recording the thermal effect. The equilibrium pressure relative to each adsorbed amount was measured by means of a differential pressure gauge (Datametrics) and the thermal effect recorded. The run was stopped at a final equilibrium pressure of 133.3 Pa. The adsorption temperature was maintained at 80 °C, in order to limit physisorption. The adsorption isotherm (relating the amount of probe gas with the corresponding equilibrium pressure) and the calorimetric isotherm (relating the integral heat of adsorption with the corresponding equilibrium pressure) were obtained from each adsorption run. Combining the two sets of data, a plot of the differential heat of adsorption as a function of the adsorbed amount was drawn, which gives information on the influence of the surface coverage on the energetics of the adsorption.

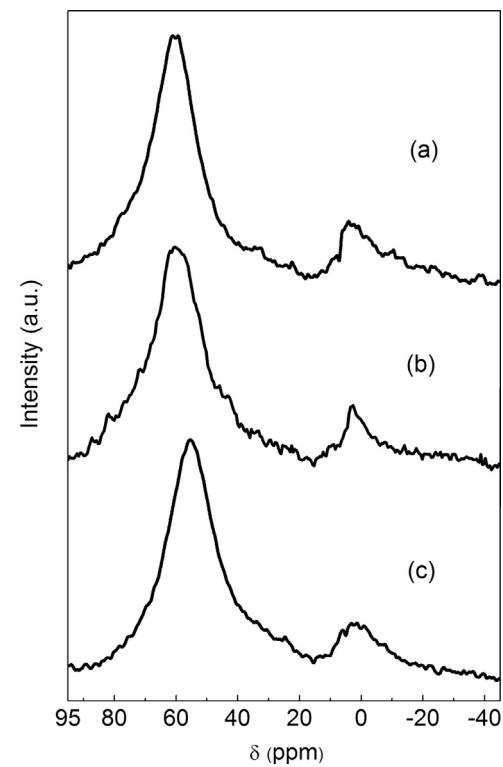


Fig. 2. ²⁷Al MAS NMR spectra for Al-SBA-15(3) (a), Al-SBA-15(22) (b), and Al-SBA-15(73) (c).

2.4. Catalytic runs

The transesterification reaction was carried out in a 100 cm³ stainless steel batch reactor (Parr 4843), equipped with intake and exhaust valves for N₂, liquid sampling valve, pressure gauge, internal thermocouple and stirrer. The reactor was fitted with a heating mantle, which allowed the achievement of a uniform temperature throughout its volume. A reaction temperature of 180 °C was considered a balanced choice, hopefully assuring the occurrence of the transesterification reaction to a significant extent while limiting the possibility that undesired reactions take simultaneously place. In view of the methanol volatility at such temperature, the runs have been carried out under a pressure of 4 MPa, which had also been adopted by other authors [9 and literature therein]. According to the literature [9 and literature therein], a high methanol to oil molar ratio (30–150:1) and large amounts of catalyst (typically >10 wt% of the reaction mixture) are often required to obtain good FAMEs yields. We tested our catalysts with a methanol/oil ratio of 12 mol/mol and 6.5 wt% of catalyst (referred to the oil + CH₃OH mass) with a double aim: (i) to check whether their performance could be good enough even under such relatively mild conditions, which would represent an advancement in comparison with previous work in the field; (ii) to avoid possible overconversion of TGs into FAMEs since the early reaction times, which would make difficult to compare the catalysts. In the case of soybean oil, runs with CH₃OH/oil molar ratio of 30 were also carried out, as well as further experiments in the 70–250 °C range with an alcohol/oil ratio of 12 mol/mol.

In a typical run, lasting up 24 h, 1.25 × 10⁻² mol of oil and 1.50 × 10⁻¹ mol of methanol were charged into the reactor and contacted with 1 g of freshly calcined (12 h at 550 °C) catalyst (particle size below 125 μ m). No differences in the FAMEs yield (as defined in Eq. (1) below) were observed in preliminary runs carried out with a stirring speed of 200, 400 and 600 rpm, which indicated the absence of external mass transfer limitations. It was however con-

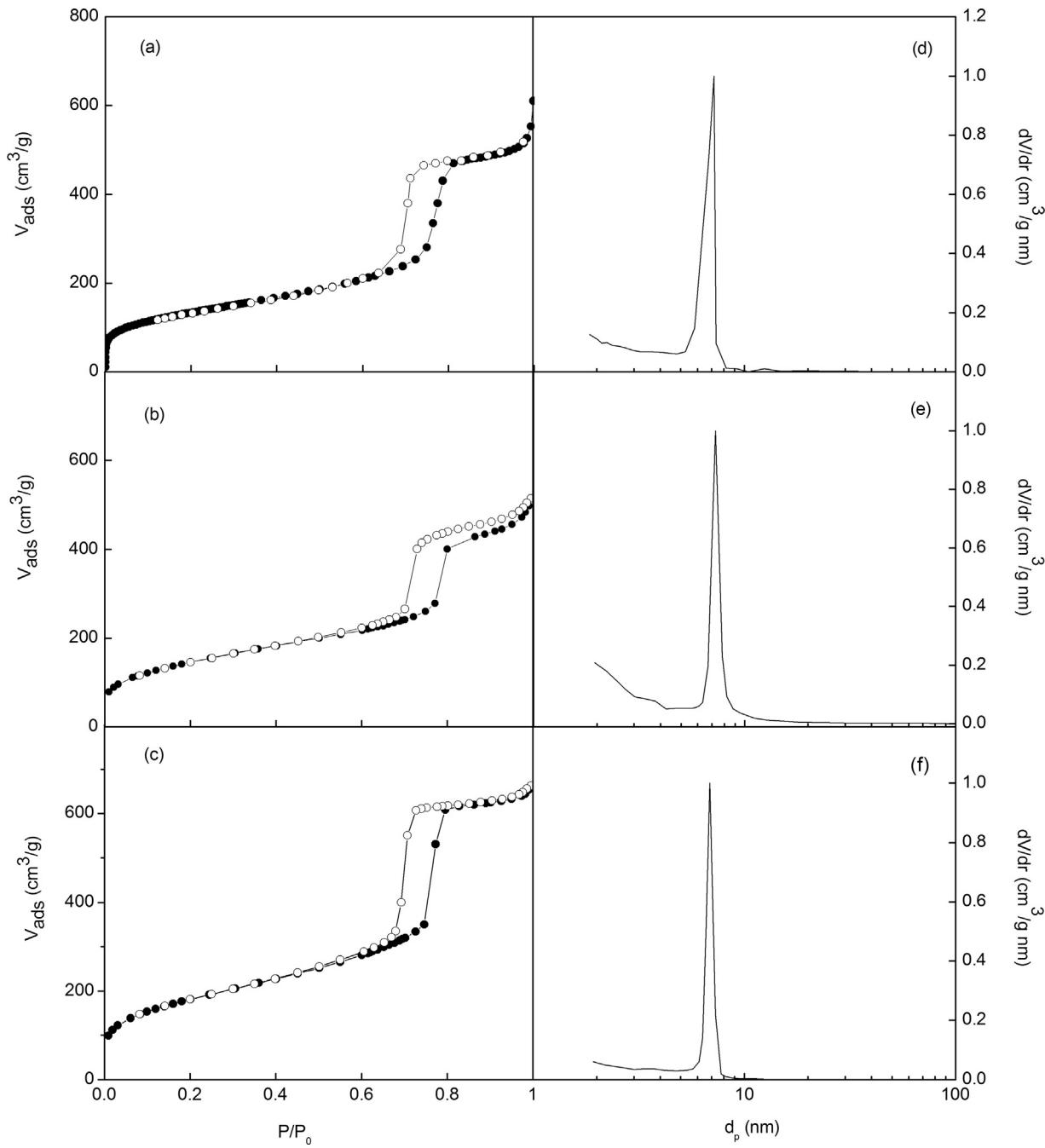


Fig. 3. Nitrogen physisorption isotherms (left side) and pore distribution plots (right side) for Al-SBA-15(3) (a, d), Al-SBA-15(22) (b, e), and Al-SBA-15(73) (c, f).

sidered safer to work at a stirring speed of 400 rpm instead of 200. Such stirring speed seemed also more appropriate than 600 rpm, in order to avoid any possible risk of spreading of the reaction mixture onto the walls of the reaction vessel. After a given reaction time, the reactor was cooled down to room temperature by immersion into an ice-bath and the sample collected in a closed vial for analysis. An HP 6890 Series on-column gas chromatograph equipped with a capillary column (MXT-Biodiesel TG from Superchrom, 15 m length, 0.32 mm ID, 0.10 μm film thickness with 2 m of 0.53 mm ID Guard) and FID was used. Helium was used as carrier gas. The temperature program of the oven was as follows: from 50 $^{\circ}\text{C}$ (hold 1 min) to 180 $^{\circ}\text{C}$ (heating rate 15 $^{\circ}\text{C}/\text{min}$), from 180 $^{\circ}\text{C}$ to 230 $^{\circ}\text{C}$ (heating rate 7 $^{\circ}\text{C}/\text{min}$) and from 230 $^{\circ}\text{C}$ to 380 $^{\circ}\text{C}$ (heating rate 30 $^{\circ}\text{C}/\text{min}$), then hold for 10 min. The temperature of the detector was set at 380 $^{\circ}\text{C}$. The reaction products were identified

by GC-MS (7820A Agilent GC coupled with 5975 Agilent MSD). The measurements were carried out by working in electron impact at 70 eV with a source temperature of 100 $^{\circ}\text{C}$. The GC details were as follows: carrier gas He, HP-5-MS capillary column (30 m length, 0.25 mm ID, 0.25 μm film thickness), oven temperature program from 150 $^{\circ}\text{C}$ to 270 $^{\circ}\text{C}$ (heating rate 15 $^{\circ}\text{C}/\text{min}$).

Methyl esters were the most abundant compounds among the reaction products (FAMEs = 56–67 and 70–80 wt% at 24 h for soybean oil and Jatropha oil, respectively). Besides glycerol and methyl esters, monoglycerides, diglycerides and FFAs were also produced during the run. The evolution of the FAMEs and FFAs content as a function of the reaction time was determined. Methyl palmitate (MeP), methyl oleate (MeO), methyl linoleate (MeL), methyl linolenate (MeLn), and methyl stearate (MeS) were monitored in the reaction mixture. Tricapryln was used as an internal standard.

Approximately 0.08 g of the reaction mixture was weighed in a vial and a sample of 500 μ L of tricapryl solution (0.1 g of tricapryl diluted to 100 cm^3 in *n*-heptane) was added. 5 μ L of this solution were functionalized with 20 μ L of MSTFA and set for 15–20 min at room temperature. For the GC analysis, 1 μ L of the functionalized sample was injected on-column and the peak areas of the compounds were integrated.

The FAMEs yield was calculated according to the following equation:

$$\text{yield(mol\%)} = \frac{\text{mass FAMEs produced/MM}_{\text{av}}\text{FAMEs}}{3 \times (\text{mass oil loaded/MM}_{\text{av}}\text{oil})} \times 100 \quad (1)$$

where MM_{av} is the experimental average molar mass and the factor 3 takes into account that each triglyceride molecule yields three methyl ester molecules.

For the determination of the FFAs content, oleic acid was used in the analysis calibration as a molecule representative of the free fatty acids. After 24 h of reaction, the acid number of the exhaust oil was also determined according to the standard ASTM D 974 procedure.

The nature of the organic material (coke) retained by the catalyst during the reaction was determined after dissolution of the spent catalyst in 40 wt% HF at room temperature, extraction in methylene chloride, almost complete evaporation of the solvent and analysis by GC-MS (7820A Agilent GC coupled with 5975 Agilent MSD) with an oven temperature program from 40 $^{\circ}\text{C}$ (hold 3 min) to 260 $^{\circ}\text{C}$ (heating rate, 40 $^{\circ}\text{C}/\text{min}$). The procedure is reported in detail elsewhere [25]. In the present case, it allows to detect the presence of those products which form during the reaction but escape determination by GC analysis, their signals being too weak and confused with the baseline noise because of the addition of a very dilute solution of internal standard prior to injection.

3. Results

3.1. Structural and textural characterization

The ICP-AES results gave total Si/Al ratios of 3.4, 22.2 and 73.4 for the three Al-SBA-15 samples, in good agreement with the gel compositions, indicating the efficiency of the preparation procedure. Accordingly, the catalysts were coded as Al-SBA(x), with $x = 3, 22$ and 73. Their low-angle X-ray diffraction patterns (Fig. 1) show three well-resolved peaks which can be indexed as the (1 0 0), (1 1 0), and (2 2 0) reflections associated with a hexagonal symmetry. These results are in agreement with the presence of a two-dimensional hexagonal P6 mm structure with a large unit-cell parameter and indicate that the structure is actually representative of a long-range order.

The ^{27}Al MAS NMR spectra of the Al-SBA(x) catalysts are shown in Fig. 2. Two resonance peaks are visible in each spectrum, at about 55 and 0 ppm, respectively. The resonance at ca. 55 ppm can be assigned [26,27] to aluminium species in tetrahedral coordination (Al_{IV}), whereas the resonance at 0 ppm can be assigned to octahedral aluminium species (Al_{VI}). Comparison of the Al_{IV} amount with the total aluminium content revealed that 90, 92 and 87% of the Al atoms are incorporated in tetrahedral positions for Al-SBA(3), Al-SBA(22) and Al-SBA(73), respectively.

The nitrogen adsorption-desorption isotherms of the Al-SBA(x) catalysts (Fig. 3a–c) can be classified as type IV and exhibit an H1-type hysteresis loop at high relative pressure, which are typical features for mesoporous materials with cylindrical channels open at both ends. The pore size-distribution plots (Fig. 3d–e) indicate for each sample a monomodal, narrow distribution centred at 6.5, 6.1 and 6.4 nm for Al-SBA(3), Al-SBA(22) and Al-SBA(73), respectively. Surface area values of 479, 519 and 638 m^2/g , and pore volume values of 0.86, 0.80 and 1.02 cm^3/g were calculated for the samples with Si/Al = 3, 22 and 73, respectively.

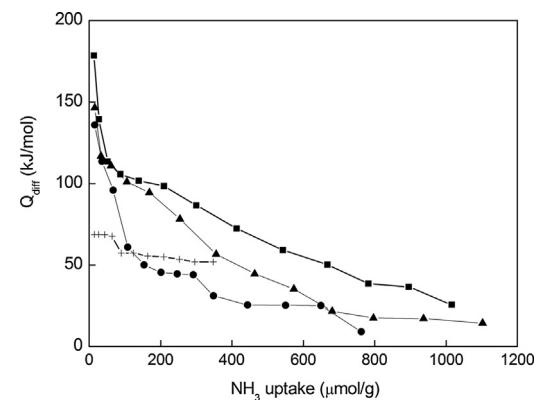


Fig. 4. Differential heat of adsorption vs. ammonia uptake at 80 $^{\circ}\text{C}$ for Al-SBA-15(3) (■), Al-SBA-15(22) (▲), Al-SBA-15(73) (●), and SBA-15 (+).

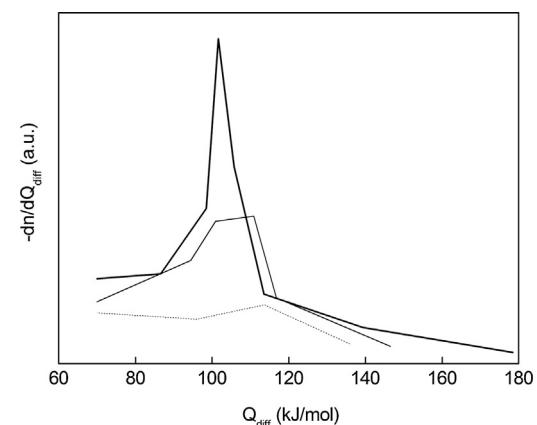


Fig. 5. Site energy distribution plots for Al-SBA-15(3) (thick line), Al-SBA-15(22) (thin line), and Al-SBA-15(73) (dotted line), as obtained by graphical derivation of Fig. 4 curves.

3.2. Microcalorimetric investigation

The calorimetric results for the Al-SBA(x) catalysts are summarised in Figs. 4 and 5. The differential heat of adsorption, Q_{diff} , is plotted vs. the ammonia uptake in Fig. 4. For all the samples Q_{diff} decreases from initial values of 136–179 kJ/mol, indicative of the presence of strong acid sites, to values as low as 9–26 kJ/mol in the high-coverage region, where non-specific ammonia adsorption might also take place. The individuation of the point at which the adsorption shifts from chemical to physical relies on an adsorption experiment carried out on an Al-free SBA-15 sample, where differential adsorption heat values as high as 69 kJ/mol are observed (Fig. 4), in agreement with previous experiments on pure silica samples [28,29]. Accordingly, the fraction of ammonia uptake for the Al-SBA(x) catalysts corresponding to differential heats below 70 kJ/mol was ascribed to non-specific hydrogen bonding and/or physical adsorption on the silica part of the catalyst, and neglected in calculating the acid sites concentration, n_A . The obtained n_A values are 438, 293, and 93 $\mu\text{mol/g}$ for Al-SBA(3), Al-SBA(22), and Al-SBA(73), respectively.

The Q_{diff} decrease with increasing NH_3 uptake indicates heterogeneity in the strength of the acid sites. The significant differences in the decreasing trend of the Q_{diff} vs. ammonia uptake curves suggest that the heterogeneous character of the sites is not the same for all the samples. The differences among them can be highlighted by considering the strength distribution profiles of Al-SBA(3), Al-SBA(22), and Al-SBA(73). These are shown in Fig. 5, where the $-\text{dn}_A/\text{d}Q_{\text{diff}}$ values obtained by graphical derivation of the curves of

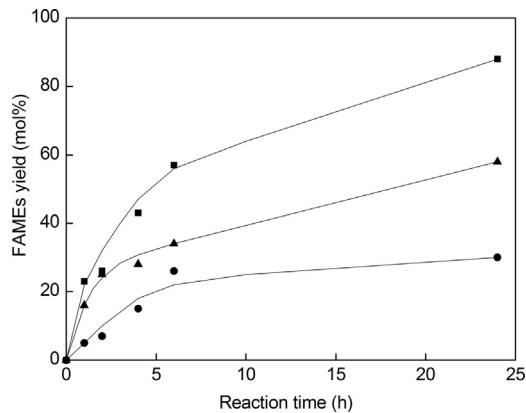


Fig. 6. FAMEs yield vs. reaction time for soybean oil transesterification at 180 °C and 4 MPa, and CH₃OH/oil molar ratio of 12 on Al-SBA-15(3) (■), Al-SBA-15(22) (▲) and Al-SBA-15(73) (●).

Fig. 4 are plotted versus Q_{diff} for the three catalysts. The energy distribution plot for Al-SBA(3) contains a relatively sharp peak centred around 102 kJ/mol. This suggests that a family of sites able to adsorb ammonia with a strength in a narrow range around 102 kJ/mol is present on this sample, the population of such sites being given by the area under the peak. A peak is also present in the energy distribution plot for Al-SBA(22), centred around 106 kJ/mol. Its lower area and enlarged shape indicate that the population of sites of this family is lower and the strength of their interaction with ammonia lies in wider range than in the case of Al-SBA(3). Concerning Al-SBA(73), the peak at 114 kJ/mol is so small and broad that it can be hardly associated to a family of sites, and the catalyst should be better considered as continuously heterogeneous as to the strength of its sites.

3.3. Catalytic runs

3.3.1. Soybean oil

The FAMEs yield obtained by reacting methanol with soybean oil in a molar ratio of 12 over the Al-SBA(x) catalysts at 180 °C and 4 MPa is reported versus the reaction time in Fig. 6. All the Al-SBA(x) catalysts are active for the oil conversion, whereas no reaction was observed over an Al-free SBA-15 sample. The best performance is observed for Al-SBA(3), over which ca. 90 mol% methyl esters yield is attained at a reaction time of 24 h. Besides glycerol and methyl esters, by far the most abundant products, also free fatty acids, whose content in the soybean oil feed is negligible (see Section 2.1), were found to form, reaching a value of 2.45–3.52 wt% at a reaction time of 24 h. The organic material adsorbed/retained in the catalysts during the reaction resulted completely soluble in methylene chloride (see Section 2.4) and was found to contain, besides FAMEs, glycerol and FFAs, also diglycerol, benzaldehyde, several aliphatic aldehydes and alcohols, 3-octen-2-one, C₈ olefins, esters with double bonds and oxo-esters. These findings suggest that a variety of undesired reactions take place, though to a minor extent, besides transesterification.

The Al-SBA(3) sample was recovered after 24 h of reaction, washed with *n*-heptane and methanol, calcined at 550 °C for 12 h, and tested again for soybean oil conversion for another 24 h. The corresponding FAMEs yield vs. reaction time is compared with that obtained over fresh Al-SBA(3) in Fig. 7. The two sets of data points are interpolated by the same curve, which indicates that the activity of the spent catalyst is fully recovered.

Fresh Al-SBA(3) samples were also used for exploring the influence of the methanol to oil molar ratio and the reaction temperature on the FAME yield. As expected, increasing the methanol/oil ratio

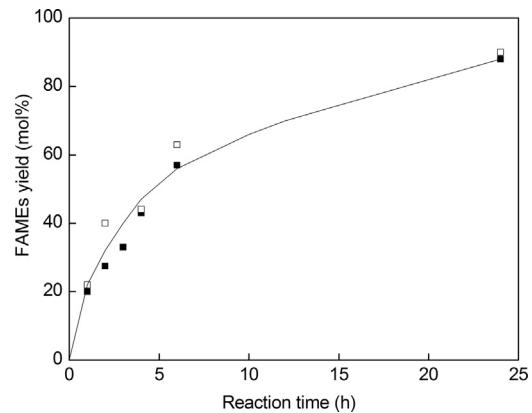


Fig. 7. FAMEs yield vs. reaction time for soybean oil transesterification at 180 °C, 4 MPa, and CH₃OH/oil molar ratio of 12 on fresh (■) and regenerated (□) Al-SBA-15(3).

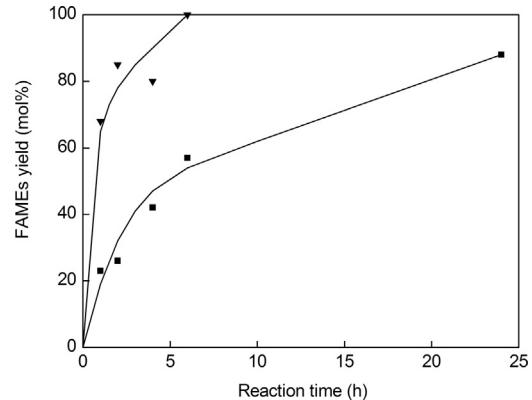


Fig. 8. FAMEs yield vs. reaction time for soybean oil transesterification at 180 °C, 4 MPa, and CH₃OH/oil molar ratio of 12 (■) and 30 (▼) over Al-SBA-15(3).

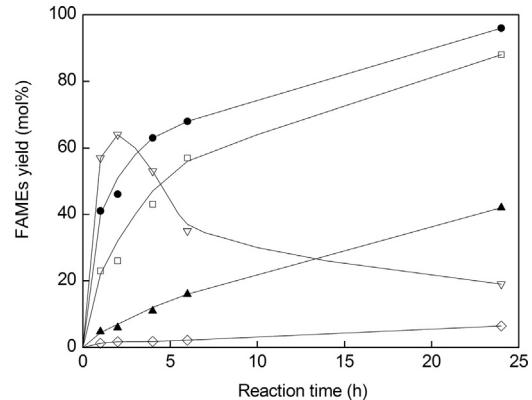


Fig. 9. FAMEs yield vs. reaction time for soybean oil transesterification at 4 MPa, and CH₃OH/oil molar ratio of 12 at 70 °C (◊), 150 °C (▲), 180 °C (□), 200 °C (●), and 250 °C (▼) on Al-SBA-15(3).

from 12 to 30 mol/mol results in an increased catalyst performance at 180 °C (Fig. 8), 100 mol% FAMEs yield being early (6 h) obtained. The influence of the temperature on the soybean oil transesterification was investigated in runs carried out on Al-SBA(3) in the 70–250 °C with a CH₃OH/oil ratio of 12 mol/mol. The pertinent FAMEs yield vs. reaction time curves are shown in Fig. 9. A remarkable increase in the methyl esters yield is observed at a reaction time of 1 h as the reaction temperature is raised from 70 °C (FAMEs yield 1 mol%) to 250 °C (FAMEs yield 64 mol%). Whatever the reaction temperature, the FAMEs yield vs. reaction time

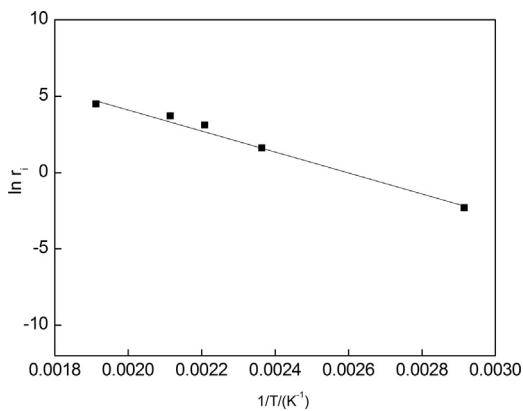


Fig. 10. Arrhenius plot for soybean oil transesterification at 4 MPa, and $\text{CH}_3\text{OH}/\text{oil}$ molar ratio of 12 on Al-SBA-15(3).

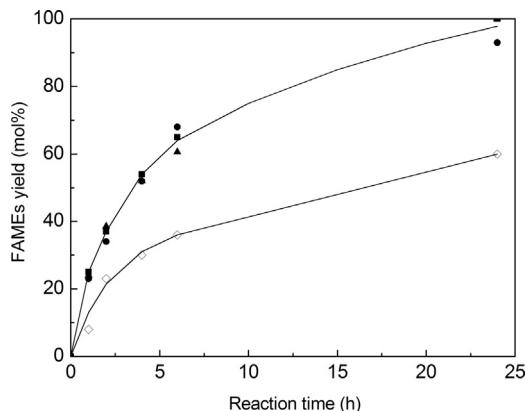


Fig. 11. FAMEs yield vs. reaction time for *Jatropha* oil transesterification at 180 °C, 4 MPa, and $\text{CH}_3\text{OH}/\text{oil}$ molar ratio of 12 on Al-SBA-15(3) (■), Al-SBA-15(22) (▲), Al-SBA-15(73) (●), and in the absence of a catalyst (◊).

curves monotonically increase, except for the run at 250 °C, whose curve dramatically grows to a maximum (64 mol% at 2 h) and then decreases (19 mol% at 24 h). This indicates that at such temperature the FAMEs resulting from the transesterification reaction rapidly undergo consecutive transformations to other products. Interestingly, after 1 h of reaction at 250 °C an FFAs content of 2.02 wt% was measured in the reaction mixture and a value as high as 24.03 wt% was determined after 24 h, whereas acidity values of 0.91–3.79 wt% were measured at 24 h for the runs at 70–200 °C. This suggests that at 250 °C free fatty acids may form to a remarkable extent through the consecutive transformation of the primary products of transesterification. The initial rate (r_i) of the transesterification reaction, expressed as mol% FAMEs yield/(h × g_{catalyst}), was calculated from the slope at zero reaction time of the curves in Fig. 9 and used for obtaining the Arrhenius plot shown in Fig. 10, which gives an activation energy of 59 ± 4 kJ/mol. Though low, such value is somewhat higher than the activation energy reported for the transesterification of triacetin with methanol [30] in sulphuric acid (46.1 kJ/mol) and Nafion SAC-13 (48.5 kJ/mol), which are the only activation energy data available in the literature on the acid-catalysed transesterification reaction.

3.3.2. *Jatropha* oil

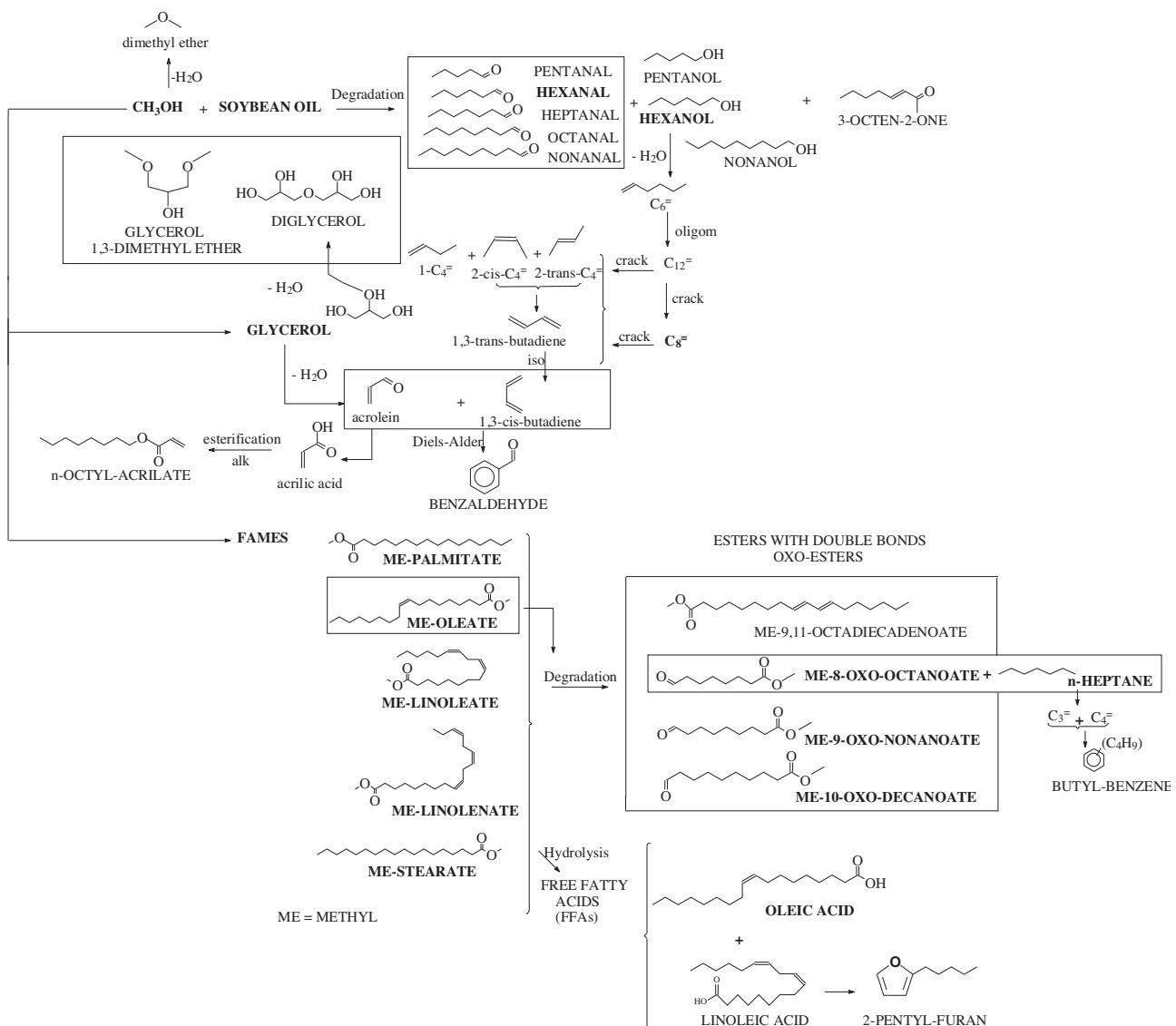
Fig. 11 summarizes the results obtained by feeding *Jatropha* oil with methanol in a molar ratio of 1:12 over the Al-SBA(x) catalysts at 180 °C and 4 MPa. The FAMEs yield vs. reaction time data reported clearly show that there are no significant differences in the performance of the three catalysts, over which a FAMEs yield of

(or very close to) 100 mol% is obtained at a reaction time of 24 h. The evolution of the free fatty acids, whose content in the *Jatropha* oil feed is 5.49 wt% (see Section 2.1), was also monitored and a residual amount of only 0.78–1.02 wt% of FFAs was detected in the reaction mixture at a reaction time of 24 h, suggesting the occurrence of their esterification by methanol. Several other reactions also occur during the *Jatropha* oil processing, as indicated by the composition of the organic material retained by the catalysts: diglycerol, several aliphatic aldehydes and alcohols, 3-octen-2-one, esters with double bonds and oxo-esters were detected besides larger amounts of FAMEs and glycerol and traces of FFAs. At variance with the case of soybean oil, benzaldehyde and C₈ olefins were lacking in the material adsorbed on the catalysts. An important feature of *Jatropha* oil is that it undergoes transformation also in the absence of a catalyst. This is shown in the same Fig. 11, where it can be seen that at 180 °C the FAMEs yield in the absence of a catalyst is significant (8 mol%) already at a reaction time of 1 h and becomes remarkable (60 mol%) after 24 h. Runs at 120 and 100 °C were also carried out, showing that in the absence of a catalyst the oil transformation was remarkably depressed at 120 °C (FAMEs yield = 1 and 13 mol% at a reaction time of 1 and 24 h, respectively) and no more occurred at 100 °C. At such temperature the Al-SBA(x) catalyst were found only slightly active, the FAMEs yield being only 10, 8 and 6 mol% over Al-SBA(3), Al-SBA(22) and Al-SBA(73), respectively, at a reaction time as high as 24 h.

4. Discussion

The results of the present work can be compared with previous findings reported in the literature on soybean oil transformation over heterogeneous acidic catalysts. A FAMEs yield of 90 mol% was claimed over zirconia/alumina-supported WO_3 catalysts at 250 °C in a flow reactor operated under atmospheric pressure with 4 g of catalyst, methanol + oil feed of 7.4 g/h and $\text{CH}_3\text{OH}/\text{oil}$ ratio of 40 mol/mol [10]. A FAMEs yield of 90 mol% is also obtained on Al-SBA(3) (Fig. 6). Though the batch conditions used in the present work require 24 h for attaining such yield, the remarkably lower values of reaction temperature (180 instead of 250 °C), catalyst amount based on the methanol + oil feed (6.4 instead of 54 wt%) and $\text{CH}_3\text{OH}/\text{oil}$ molar ratio (12 instead of 40) seem to indicate a better performance of the present catalyst. Note that over the latter, if the methanol to oil molar ratio is increased to 30, 100 mol% FAMEs yield is early reached (6 h) (Fig. 8). Very high FAMEs yields (92–99 mol%) were obtained in batch over sulphated zirconia catalysts [11] under milder conditions (1 h of reaction at 120 °C, autogenic pressure, 1–10 wt% of catalyst with respect to the oil mass, $\text{CH}_3\text{OH}/\text{oil}$ molar ratio = 20) than those used in the present work. Such better performance of sulphated zirconia is however only apparent, as leaching of the active phase rapidly occurred. The superiority of Al-SBA(3) in comparison with ion-exchange [12] and sulphonated resins [13], which were tested at a temperature as low as 60 °C because of their low thermal stability, is manifest from their negligible or very low activity. FAMEs yield did not exceed 49 mol% over La³⁺-exchanged Beta zeolites at 60 °C [14] or 22–40 mol% over protonic Beta zeolites of diverse Si/Al ratios at 180 °C [15], reasonably because of hindered diffusion of the triglycerides. Interestingly, results comparable to those for the present Al-SBA(x) catalysts were observed over protonic hierarchical zeolites of diverse Si/Al ratios (FAMEs yields 50–70 mol% after 24 h of reaction under conditions identical to those used in the present work) [15]. This supports the view that in both cases the favoured transport of the reactants inside the mesopore system is quite an important factor, among others, for the good performance of the catalysts.

The FAMEs production by TGs transesterification with methanol occurs through a stepwise pathway in which the triglyceride



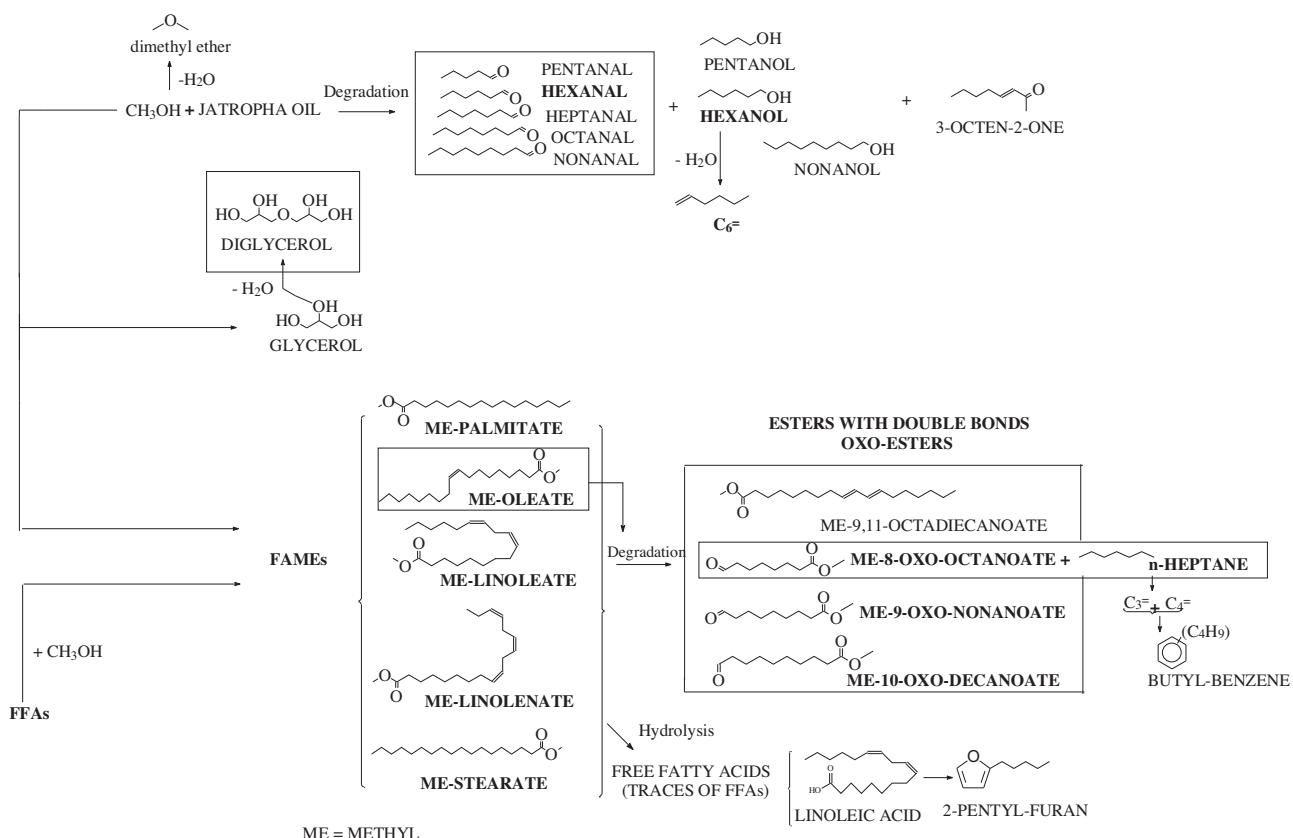
Scheme 1. Organic compounds retained by the catalysts during soybean oil reaction and their formation pathways. The compounds actually identified by GC–MS are reported in capital, the most abundant in bold.

molecule is first converted to diglyceride, then to monoglyceride and finally to glycerol, a molecule of methyl ester being released in each step. The acid-catalysed reaction is initiated by the interaction of the acid with the carbonyl group of the glyceride, which results in an increased positive charge on the carbonyl carbon and makes it prone to the nucleophilic attack by the alcohol [31,32]. According to the literature [33], literature therein], both Brønsted and Lewis acids are able to catalyse the reaction. It is generically stated that a requirement for a good solid-acid catalyst is an appropriate site strength [9] and by analogy with the catalysis operated by sulphuric acid in homogeneous medium it is inferred that the acid sites should be quite strong. However, a clear-cut distinction between good catalysts with strong acid sites on the one hand and poor catalysts with weak acid sites on the other is probably an oversimplification. For instance, a too high strength of the acid sites is reported as detrimental in the case of heterogeneous Lewis acid catalysts, due to the disfavoured desorption of the new ester formed after the nucleophilic attack step [33], literature therein].

The role of the catalyst acidity has been specifically addressed in the present work. Concerning the nature of the active sites, though adsorption microcalorimetry is unable to discriminate between

Brønsted and Lewis acidity, some clues can be obtained by the NMR results. These indicate (Section 3.1) that on the Al-SBA(χ) catalysts bridging hydroxyl groups, Al–O(H)–Si, associated to Al_{IV} atoms [34] and acting as Brønsted sites, are by far the most abundant. Al species in which Al atoms are in octahedral coordination (Al oxides and/or Al oxohydroxides), acting as Lewis and/or Brønsted sites, account for ca. 10% of the total Al content. The conclusion can be drawn that the contribution of Lewis sites to the overall acidity of the present catalysts is very low. Accordingly, if the Lewis sites were the only sites able to catalyse the soybean oil transesterification, a very low FAMEs yield would be observed, even assuming that all the Lewis sites were of appropriate strength. This is in contrast with the experimental evidence (Fig. 6), which shows that even the catalyst with the highest Si/Al ratio is able to catalyse the transesterification reaction to a significant extent. It hence seems that the major role in promoting soybean oil transesterification over the present catalysts is played by Brønsted sites.

As shown in Fig. 12, a good linear correlation ($R=0.994$) exists between the initial activity for the soybean oil transesterification and the overall concentration of the acid sites, n_A (i.e., the ammonia-adsorbing sites with $Q_{\text{diff}} > 70 \text{ kJ/mol}$, Section 3.3.2). However, plots



Scheme 2. Organic compounds retained by the catalysts during *Jatropha* oil reaction and their formation pathways. The compounds actually identified by GC-MS are reported in capital, the most abundant in bold.

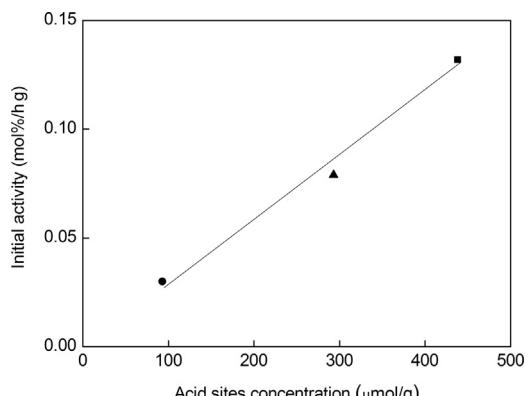


Fig. 12. Initial activity vs. acid sites concentration for soybean oil transesterification at 180 °C, 4 MPa, and CH_3OH /oil molar ratio of 12 on Al-SBA-15(3) (■), Al-SBA-15(22) (▲), and Al-SBA-15(73) (●).

of the initial transesterification activity vs. the population of sites stronger than 75, 80, 85, 90, 95, and 100 kJ/mol (calculated from calorimetric data) were found linear as well, with quite similar correlation factors ($R = 0.988-0.993$, Figs. 1–6S in Supplementary material). Though a bit poorer ($R = 0.982$), a linear correlation (Fig. 7S in Supplementary material) was also obtained in a plot of the initial transesterification activity vs. the population of relatively homogeneous sites of strength around 102–114 kJ/mol (calculated from the peak areas in Fig. 5). Apparently, this prevents from discriminating whether the soybean oil transesterification is catalysed by all the acid sites, by those stronger than 75, 80, 85, 90, 95, or 100 kJ/mol, or by those belonging to a relatively homogeneous family of 102–114 kJ/mol. However, as the FFAs-containing *Jatropha*

oil undergoes transformation even in the absence of the solid catalyst, it is manifest that even carboxylic acids of such a weak acidic strength as the FFAs are able to catalyse, besides their own esterification (the FFAs content decreases with reaction time, Section 3.3.2), also TGs transesterification (the FAMEs yield grows up to to the remarkable value of 60 mol% after 24 h, Fig. 11). The conclusion can hence be drawn that all the acid sites present on Al-SBA(x) catalysts are involved in the soybean oil transesterification, whatever their strength.

Autocatalytic effects arising from the weak acidity of the carboxylic acids themselves have been discussed for the esterification of acetic acid with methanol in [35]. Acetic acid can in principle catalyse its own esterification either by directly attacking a second acid molecule or by releasing protons which then attack a CH_3COOH molecule. In either case, the protonated species undergoes nucleophilic attack by methanol, with formation of a tetrahedral intermediate which then disproportionates giving the ester. Undissociated acid protolysis is probably the dominating route in the case of the FFAs present in the *Jatropha* oil, in view of the lack of water in the feed and the weak dissociation of the acids in pure methanol. Concerning the influence of the feed acidity on the transesterification reaction, FAMEs formation in the absence of a catalyst has been reported during crude palm kernel and coconut oils processing [18]. Both the oils are acidic (FFAs content = 1.05 and 2.25 wt% as lauric acid, respectively) and FAMEs yields as high as 30 and 41 wt%, respectively, were observed with a reaction time of 4 h at 200 °C, 5 MPa and methanol to oil ratio of 6 mol/mol. Upon addition of a solid catalyst (zirconia, zinc oxide, sulphated tin oxide and sulphated zirconia; 3 wt%, based on the oil mass), an increase in the FAMEs yield to ca. 65–95 wt% and ca. 49–86 wt% for palm kernel oil and coconut oil, respectively, was observed at a reaction time of 4 h. Accordingly, the catalyst performance was evaluated

by subtracting the results for the blank run from those of the solid-catalysed run. For *Jatropha* oil, a remarkable increase in the FAMEs yield in the presence of Al-SBA(x) catalysts is also observed, as a result of the occurrence of the reaction also on the acid sites of the solid. The interesting point however is that the performance of the three Al-SBA(x) catalysts is virtually the same (Fig. 11), in spite of their remarkable differences in terms of both concentration and strength distribution of the acid sites (see Section 3.2). It is worthy of note that for soybean oil, whose FFAs content is negligible, the differences in the acid features of the three Al-SBA(x) catalysts are clearly reflected in their different transesterification performance (Fig. 6). Apparently, in the case of *Jatropha* oil, the catalytic effect stemming from the presence of FFAs and that originated by the acid sites of the solid are not simply additive. Rather, they seem involved in a complex (undisclosed) interplay, which levels out the catalyst performance. It is also worthy of note that when the homogeneously catalysed reaction is completely suppressed, i.e., at 100 °C, the solid-catalysed reaction is depressed to such an extent (FAMEs yields at 24 h are 10, 8 and 6 mol% for Al-SBA(3), Al-SBA(22) and Al-SBA(73), respectively) that any performance-based comparison of the catalysts is unreliable.

As already mentioned in Section 3.3.1, the presence of increasingly high amounts of FFAs in the soybean oil reaction mixture along with reaction time and the findings on the nature of the organic material retained by the catalysts suggest the simultaneous occurrence, besides transesterification, of several secondary reactions. Plausible pathways for the transformations undergone by soybean oil are sketched in Scheme 1, where the products actually detected in the reaction mixture or in the organic material retained by the catalyst are indicated in bold characters. The reliability of Scheme 1 is supported by specific findings of other authors in reaction contexts different from transesterification, as discussed below. FFAs would be originated through the acid-catalysed FAMEs hydrolysis by the water resulting from either methanol dehydration to dimethyl ether and glycerol double dehydration to acrolein. The reactant alcohol dehydration has been reported to occur at 100–140 °C [9,36] and is hence plausible also in the present case. According to the patent literature on acrolein production [37], also glycerol double dehydration can take place under mild condition, though quite high temperatures (>250 °C) would be required for its occurrence to a high extent [9,38,39]. In agreement with [40–42], the observed formation of products such as methyl-9,11-octadecadienoate, methyl-8-oxo-octanionate, methyl-9-oxo-octanionate, and methyl-10-oxo-octanionate would occur through the thermal decomposition of FAMEs. Aldehydes (C₅–C₉) and alcohols (C₅, C₆, and C₉), among which hexanal and 1-hexanol are the main compounds, would be originated by the thermal decomposition of soybean oil, in agreement with [43,44]. The C₈ olefins (3,5-octadiene and *n*-octene) detected in the material extracted from the catalysts would form through the acid-catalysed transformation of hexanol to hexene, followed by oligomerization to C₁₂ olefins, which would then crack to C₄ and C₈ alkenes. This is suggested by literature results showing that: (i) 1-, 2-, and 3-hexene can be obtained from 1-hexanol over acidic resins and beta zeolites in liquid phase at 150–190 °C [45]; (ii) at 200 °C and 5 MPa, HZSM-5 zeolites, as well as Al-MCM-41 and Al-SBA-15 mesoporous aluminosilicates, are able to catalyse the formation of oligomers from C₆ olefins and their cracking to C₄ and C₈ alkenes [46]. Concerning the presence of benzaldehyde among the products retained by the catalysts, it would be the result of a Dies–Alder reaction involving 1,3-*cis*-butadiene originating through the hexane oligomerization-cracking pathway and acrolein coming from the acid-catalysed glycerol double dehydration.

Based on Scheme 1, the peculiar issues of the soybean oil transformation at 250 °C (presence of a maximum in the FAMEs yield vs. reaction time curve, Fig. 9, and FFAs content remarkably increasing

with reaction time, Section 3.3.1) in comparison with those of the runs in the 70–200 °C range (monotonic increase of FAMEs yield and very low FFAs formation during the run) can be tentatively explained. The FAMEs obtained as primary products from transesterification undergo consecutive transformation through thermal degradation and hydrolysis, which occur in parallel. As far as the soybean oil is processed at low temperatures, thermal degradation is expected to occur to a limited extent. As to hydrolysis, it is dependent on the water forming through double dehydration of glycerol to acrolein, a reaction that, according to the patent literature on acrolein production [37], takes place to a limited extent under mild conditions. This is supported by the finding that FFAs, which are virtually absent in the feed, actually form when soybean oil is processed at 70–200 °C, but their amount remains low (0.9–3.8 wt% at 24 h). Though the rate of FAMEs formation from TGs is bound to decrease with the reaction time while the rate of FAMEs consumption through thermal degradation and hydrolysis is bound to increase, at 70–200 °C the former would remain higher than the latter over the whole duration of the run. As a result, the FAMEs yield is seen to increase monotonically with reaction time with a decreasing slope. By converse, at 250 °C the extent of double dehydration of glycerol to acrolein becomes quite high, as known from the literature on acrolein production [9,38,39], thus enhancing FAMEs hydrolysis. (An increase in the FFAs content up to 24 wt% at 24 h is actually observed). Also the FAMEs thermal degradation would be reasonably enhanced at 250 °C. Apparently, the decrease in the rate of FAMEs formation and the simultaneous increase in the rate of FAMEs consumption would be such that there would be a point during the run at which the two rates become identical, appearing as a maximum in the FAMEs yield vs. reaction time curve.

Based on the evolution in the composition of the reaction mixture with reaction time and the nature of the organic material extracted from the catalysts after reaction (Section 3.3.2), an outline of the several reactions involved in the transformation of *Jatropha* oil is given in Scheme 2. Typical issues of the *Jatropha* oil in comparison with soybean oil are (i) the above-discussed occurrence of FFAs esterification in parallel to TGs transesterification and (ii) the lack of both glycerol double dehydration to acrolein and olefins formation from hexanol, highlighted by the absence of benzaldehyde among the products extracted from the exhaust catalysts. The reasons underlying the (ii) finding remain undisclosed.

5. Conclusions

The isomorphical substitution of Al atoms for Si atoms during the pH-adjusted synthesis of SBA-15 in presence of aluminium nitrate yields mesostructured, high-area, acidic catalysts. By changing the Si/Al ratio (3, 22 and 73), both the concentration of the acid sites and the site-strength distribution are remarkably modified.

The differences in the acid features reflect upon the soybean oil transesterification activity, the initial transesterification rate being dependent on the overall acid sites concentration. The apparent activation energy for the soybean oil transesterification over the catalyst with Si/Al = 3 is 59 kJ/mol. Such catalyst is the best-performing one: a FAMEs yield as high as 90 mol% being achieved at a reaction time of 24 h with a methanol to oil ratio of 12, and 100 mol% FAMEs yield being much earlier (6 h) obtained with a methanol to oil ratio of 30. It seems also better than other heterogeneous acidic catalyst so far reported in the literature. Besides transesterification, soybean oil undergoes several secondary reactions during the run. These include acid-catalysed FAMEs hydrolysis to FFAs (by the water resulting from methanol dehydration and glycerol double dehydration), thermal decomposition of FAMEs to esters with double bonds and oxo-esters, thermal degradation of soybean oil to aldehydes and alcohols, followed by

acid-catalysed alkene formation, oligomerization and cracking, and Dies–Alder Benzaldehyde formation.

Very high FAMEs yields (ca. 100 mol% at a reaction time of 24 h, with methanol to oil ratio of 12) are obtained by reacting *Jatropha* oil over the three catalysts. Their performance is virtually identical, in spite of the remarkable differences in terms of both concentration and strength distribution of the acid sites. The esterification of the FFAs present in the feed occurs in parallel to TGs transesterification. Besides the acid sites of the catalyst, also the free fatty acids present in the feed catalyse both reactions, autocatalytic FFAs esterification and TGs transesterification being observed also in absence of the solid catalysts. Apparently, the homogeneous and heterogeneous catalytic effects are not simply additive; rather, they seem to combine in such a way to level out the catalyst performance. The underlying reasons remain undisclosed. The homogeneous reactions can be suppressed by decreasing the reaction temperature to 100 °C, a temperature at which, however, the solid-catalysed reaction is depressed to such an extent (FAMEs yields at 24 h, 10–6 mol%) that any performance-based comparison of the catalysts is unreliable. Several secondary reactions occur also during the transformation of *Jatropha* oil, the difference with soybean oil being the lack of both glycerol double dehydration and olefins formation.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.11.038>.

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